Dissolved Pesticide Concentrations Detected in Storm-Water Runoff at Selected Sites in the San Joaquin River Basin, California, 2000–2001

By James L. Orlando, Kathryn M. Kuivila, and Andrew Whitehead

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CONVERSION FACTORS AND SYMBOLS

CONVERSION FACTORS

| Multiply | Ву | To obtain |
|-------------------------------------|--------|-------------------|
| kilogram (kg) | 2.205 | pound avoirdupois |
| kilometer (km) | 0.6214 | mile |
| liter (L) | 33.82 | ounce, fluid |
| meter (m) | 1.094 | yard |
| square kilometer (km ²) | 247.1 | acre |

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows: °C=(°F-32)/1.8.

ABBREVIATIONS

Bodega Marine Laboratory **BML**

GC/MS gas chromatography-mass spectrometry

milliliter mL

ng/L nanogram per liter USGS

U.S. Geological Survey

Dissolved Pesticide Concentrations Detected in Storm-Water Runoff at Selected Sites in the San Joaquin River Basin, California, 2000–2001

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ABSTRACT

As part of a collaborative study involving the United States Geological Survey Toxics Substances Hydrology Project (Toxics Project) and the University of California, Davis, Bodega Marine Laboratory (BML), water samples were collected at three sites within the San Joaquin River Basin of California and analyzed for dissolved pesticides. Samples were collected during, and immediately after, the first significant rainfall (greater than 0.5 inch per day) following the local application of dormant spray, organophosphate insecticides during the winters of 2000 and 2001. All samples were collected in conjunction with fish-caging experiments conducted by BML researchers. Sites included two locations potentially affected by runoff of agricultural chemicals (San Joaquin River near Vernalis, California, and Orestimba Creek at River Road near Crows Landing, California, and one control site located upstream of pesticide input (Orestimba Creek at Orestimba Creek Road near Newman, California). During these experiments, fish were placed in cages and exposed to storm runoff for up to ten days. Following exposure, the fish were examined for acetylcholinesterase concentrations and overall genetic damage. Water samples were collected throughout the rising limb of the stream hydrograph at each site for later pesticide analysis. Concentrations of selected pesticides were measured in filtered water samples using solid-phase extraction (SPE) and gas chromatography-mass spectrometry (GC/MS) at

the U.S. Geological Survey organic chemistry laboratory in Sacramento, California. Results of these analyses are presented.

INTRODUCTION

The land and water resources of California's San Joaquin River Basin help support the nation's most productive agricultural economy. The counties of the San Joaquin River Basin produced a variety of crops worth over 8.3 billion dollars in the year 2000 (California Department of Food and Agriculture, 2001). Important crops that are grown in this region include almonds, apricots, cherries, peaches, and walnuts. Organophosphates and other types of pesticides are applied to these orchards during dormancy to control wood-boring insects. Application of pesticides during the December–February dormant spray season coincides with the region's peak annual rainfall. Previous studies have shown that, for areas within the basin, the first significant rainfall and runoff following the winter application of organophosphate insecticides is accompanied by a rise in the detected concentrations of these same pesticides in downstream surface waters (Kuivila and Foe, 1995; Kratzer, 1997; Dubrovsky and others, 1998). Studies have also shown these pesticide pulses to be acutely toxic to certain aquatic invertebrates such as Ceriodaphnia dubia (Foe and Connor, 1991: Kuivila and Foe, 1995). However, little is known concerning the potential effects of these pulses on fish.

In 1999, the U.S. Geological Survey (USGS) Toxics Project began a collaborative study with researchers from the U.C. Davis Bodega Marine Laboratory (BML) that focused on an examination of

the physical and genetic responses to pesticides of the native California fish species, Catastomus occidentalis, under both field and laboratory conditions. Field experiments exposing C. occidentalis to storm-water runoff at three locations in the San Joaquin River Basin (fig. 1) were conducted in the winters of 2000 and 2001. During these experiments, fish were placed in cages and exposed to in-stream conditions for periods ranging from one to ten days, beginning prior to the onset of the first significant rainfall and runoff following the local application of dormant spray pesticides, and extending through the rising limb of the stream hydrograph at each site. Water samples were collected throughout the exposure periods for pesticide analysis, and laboratory fish-exposure studies. Following exposure in the field, fish were dissected and samples of blood and tissue were collected and analyzed at BML for acetylcholinesterase concentrations and overall genetic damage.

Purpose and Scope

As part of this study, the Toxics Project was responsible for a number of field and analytical tasks. These tasks included the selection of sampling sites, initiation of field experiments, collection of water samples for lab exposures and water quality analysis, and analysis of all water samples for dissolved pesticides. This report describes the sampling sites chosen and the methods and procedures used during water sample collection and analysis. Dissolved pesticide concentrations analyzed in water samples collected during this study are presented.

Acknowledgments

The authors gratefully acknowledge G. Edward Moon, of the USGS Toxics Project as well as other USGS personnel for help with sample collection and logistical support during this project. The authors also wish to acknowledge Jacqueline Houston and Theresa Pedersen of the USGS for their many hours of laboratory work and pesticide analyses. This project was funded by the USGS Toxics Substances Hydrology Program and by a grant from the U.S. Environmental Protection Agency (R-826603-01-0).

STUDY DESIGN AND METHODOLOGY

Selection of Sampling Sites

Three sites were chosen in the San Joaquin River Basin for combined fish exposure studies and pesticide analysis (fig. 1; table 1). Sites were selected on the basis of local agricultural practices, past and current use of organophosphate insecticides, previous surfacewater detections of organophosphate insecticides, suitability for fish caging, and safety of field personnel during storm conditions. Using these criteria, two sites potentially affected by insecticides were chosen: San Joaquin River near Vernalis, California (or "Vernalis"), and Orestimba Creek at River Road near Crows Landing, California (or "Orestimba"). In addition, a single control site located upstream of potential pesticide input, Orestimba Creek at Orestimba Creek Road near Newman, California (or "Upper Orestimba") was chosen (fig. 1). All three sites are located in proximity to active USGS gaging stations.

Vernalis is located at the basin outlet of the San Joaquin River watershed and receives runoff from approximately 19,002 km² of land in the Sierra Nevada, the San Joaquin Valley, and the Coast Ranges. Land use at lower elevations is principally agricultural and urban, while higher elevations are dominated by forest and woodland. This site has a long history of water-quality monitoring by numerous state and federal agencies. Previous studies have detected diazinon at concentrations in excess of 1,000 ng/L in water samples collected at this site (Kuivila and Foe, 1995). Orestimba is located approximately 1.5 km upstream from the confluence of Orestimba Creek and the San Joaquin River and represents a watershed of approximately 603 km² in the San Joaquin Valley and the Coast Ranges. Land use in the vicinity of this site is predominantly agricultural. High concentrations of agricultural chemicals have been detected at this site in previous years (Panshin and others, 1998). Upper Orestimba is located 19 km upstream of Orestimba, at the edge of the Coast Ranges. The drainage area above this site is approximately 332 km². Vegetation upstream of the sampling site is mostly woodland with little or no agriculture.

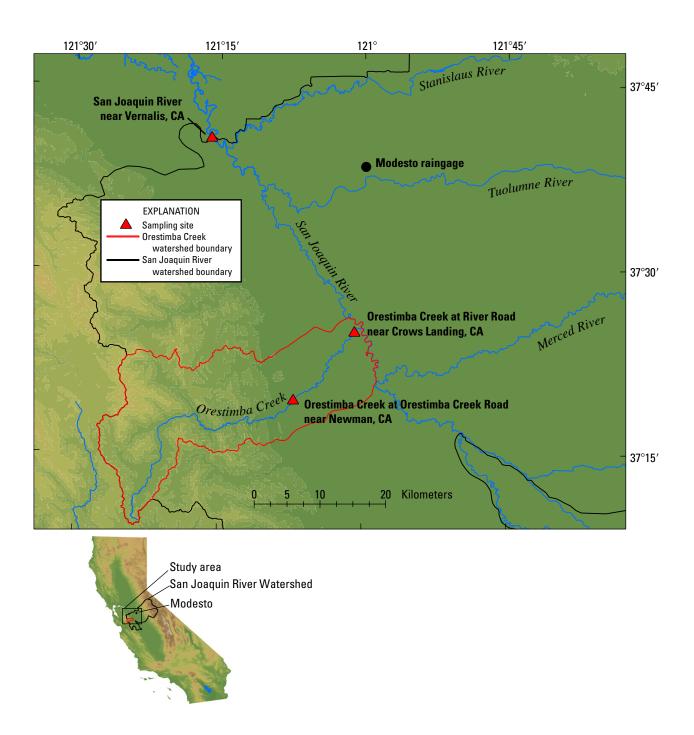


Figure 1. Location of study area and sampling sites in the San Joaquin Valley, California.

Table 1. Pesticide sampling sites, San Joaquin River Basin, California

[ID, identification; USGS, U.S. Geological Survey; km, kilometer]

| Site name | USGS site ID number | Latitude | Longitude | Description |
|---|---------------------|-----------|------------|--|
| Orestimba Creek at Orestimba Creek Road near Newman, California (Upper Orestimba) | 371912121071201 | 37°19′09″ | 121°07′15″ | Located 19 km upstream of Orestimba, at the edge of the Coast Ranges |
| Orestimba Creek at River Road near Crow's Landing, California (Orestimba) | 11274538 | 37°24′51″ | 121°00′54″ | Located 1.6 km upstream of confluence with San Joaquin River |
| San Joaquin River near Vernalis, California (Vernalis) | 11303500 | 37°40′33″ | 121°15′55″ | Basin outlet for the San Joaquin River watershed |

Generalized Sampling Methods

Field experiments were initiated just prior to the first significant rainfall (>0.5 in./day) and runoff following the local application of dormant spray pesticides in 2000 and 2001. Fish cages were emplaced at each of the sites under prestorm streamflow conditions and exposed throughout the rising limb of the stream hydrograph (figs. 2 and 3). This sequence of events was chosen to ensure the exposure to maximum concentrations of dissolved pesticides associated with initial storm runoff from upstream agriculture. Water samples for pesticide analysis and laboratory exposures were collected over the same time periods, but under varying schedules depending on the hydrologic characteristics of the individual watersheds.

All samples were collected as surface grabs by one of three methods. At Vernalis and Orestimba, samples were collected from a bridge as mid-channel surface grabs or by pumping. At Upper Orestimba, all samples were collected as mid-channel grabs or from the shore. All water samples were collected in proximity to the fish exposure cages at each site and at a depth of 0.5 m beneath the water surface. Streamflow at each site was likely well mixed, with the exception of the Upper Orestimba in 2001.

Sampling Methods at the Three Sites

Vernalis

Water samples were collected over a period of nine consecutive days (2/11/00–2/19/00) in 2000 (fig. 2) and seven consecutive days (1/26/01–2/01/01)

in 2001 (fig. 3). Additional samples were collected during the emplacement and removal of individual fish cages. Samples were obtained either by pumping directly into 1-L amber glass bottles using a peristaltic pump equipped with a single stainless steel and Teflon inlet hose suspended in mid-channel, or as single mid-channel grabs using a weighted 3-L Teflon bottle sampler from a bridge.

Orestimba

In both years, sampling took place in two stages: an initial intensive period during which samples were collected hourly over approximately 24 hours, followed by daily sampling for a period of six consecutive days (figs. 2 and 3). Additional samples were collected in 2001 during the emplacement and removal of individual fish cages. During the initial hourly sampling, water was collected using a peristaltic pump with a single stainless steel and Teflon inlet hose suspended in the center of flow. Samples were pumped directly into 1-L amber glass bottles. For the 2000 sampling period, daily water samples were collected using a weighted two-bottle sampler, which consisted of a 7-kg brass sounding weight modified to hold two 1-L amber glass bottles. During 2001, daily samples were collected using a weighted 3-L Teflon bottle sampler and poured directly into 1-L amber glass bottles. A series of samples were collected January 24–27, 2000, in response to a storm that failed to produce significant runoff. This storm was considered a "false start," though the pesticide analyses are included in this report. A complete sampling and field caging was conducted in mid-February following a much stronger winter storm.

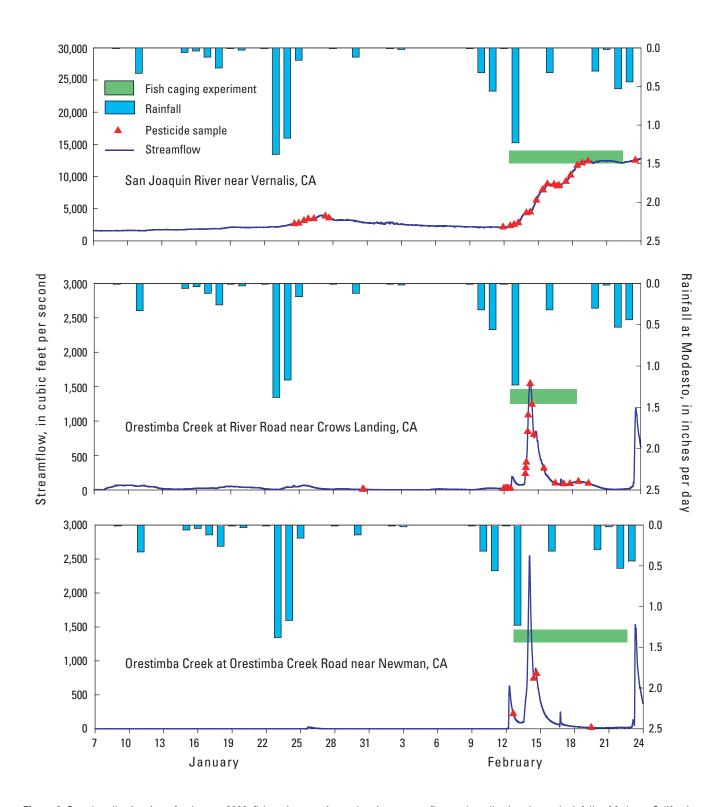


Figure 2. Sample collection times for the year 2000, fish caging experiment durations, streamflow at the collection site, and rainfall at Modesto, California. Streamflow data collected at USGS site 11274500 Orestimba Creek near Newman, California.

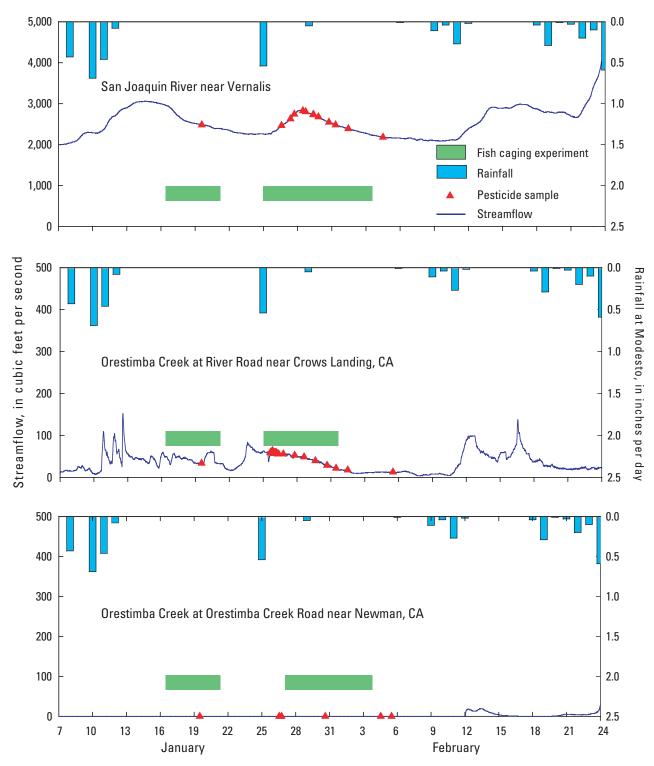


Figure 3. Sample collection times for the year 2001, fish caging experiment durations, streamflow at the collection site, and rainfall at Modesto, California. Streamflow data collected at USGS site 11274500 Orestimba Creek near Newman, California.

Upper Orestima

As a control, samples were collected at times corresponding to the beginning, middle, and end of the sampling periods of the other two sites. In 2000, all samples were collected at a point near the center of flow using a weighted two-bottle sampler. Because of very light rainfall in the upper reaches of the watershed during the 2001 sampling period, no appreciable surface flow occurred at this site. However, samples were collected from a large, permanent, in-channel pool located approximately 100 m downstream from the standard collection site. Samples were collected at times corresponding to the emplacement and removal of fish cages by submerging 1-L amber glass bottles to a depth of 0.5 m for filling.

Sample Processing and Analysis

Collected water samples were preserved on ice and, within 24 hours, filtered through baked, 0.7 micrometer glass-fiber filters. A surrogate compound, terbuthylazine, was added to provide quantitative data on extraction efficiency, and the samples were then extracted using C8 solid-phase extraction cartridges. The cartridges were then dried using a syringe to repeatedly force air through each cartridge, frozen, and delivered to the USGS organic chemistry laboratory in Sacramento, California, where they were stored frozen for up to six months. Once removed from storage, each cartridge was eluted with 9 mL ethyl-acetate and analyzed by gas chromatography-mass spectrometry (GC/MS). Samples collected in 2000 were analyzed for 26 individual pesticides, whereas in 2001, the total was 31 pesticides.

Four types of quality-control data were collected: field and laboratory equipment blanks, replicate samples, matrix spikes, and surrogate recovery. Equipment blanks were analyzed every

20–30 samples for a total of two blanks in 2000 and three in 2001. None of the pesticides were detected in the blanks. Replicate samples constituted 33 percent of the samples analyzed and were within 25 percent agreement for each of the pesticides detected. As part of the method validation, recoveries of matrix spikes were determined in 10 percent of the samples, and details are listed in the method reports (Kathryn Kuivila and Jacqueline Houston, USGS, Sacramento, California, unpub. data, 2002; Theresa Pedersen and Kathryn Kuivila, USGS, Sacramento, California, unpub. data, 2002). Recovery of the surrogate, terbuthylazine, was used to assess the efficiency of each extraction. The average percent recovery and standard deviation for terbuthylazine was calculated for each year. Sample data were excluded if the recovery of terbuthylazine was outside the control limit of the annual mean plus or minus two standard deviations (Kuivila and Houston, unpub. data, 2002; Pedersen and Kuivila, unpub. data, 2002).

DISSOLVED-PESTICIDE CONCENTRATIONS

This report presents dissolved-pesticide concentrations analyzed in water samples collected during storms in January-February 2000 and 2001. Samples were collected at three surface-water sites in conjunction with fish-caging studies (figs. 2 and 3). A total of 105 water samples were analyzed for 26 or 31 pesticides by GC/MS at the U.S. Geological Survey's organic chemistry laboratory in Sacramento, California. Results of these analyses are presented in tables 2, 3, and 4. Table 5 shows pesticide detection limits for the analysis methods used in 2000 and 2001. Pesticides that were detected at concentrations below the method detection limits listed in table 5 are shown in parentheses because the values are estimates.

 Table 2.
 Pesticide concentrations in water samples collected at Orestimba Creek at Orestimba Creek Road near Newman, California, 2000–2001.

[Values are reported as nanograms per liter. Water samples were analyzed for the following pesticides that were not detected at this site: alachlor, atrazine, azinphos-methyl, butylate, carbaryl, cyanazine, cycloate, diethatyl-ethyl, eptam, ethalfluralin, fonofos, malathion, methylparathion, napropamide, pebulate, pendimethalin, phosmet, sulfotep, and thiobencarb. nd, nondetection; —, not analyzed; (), concentration below detection limit]

| Date (mm/dd/yy) | Time | Carbo- furan | Chlor- pyrifos | Dacthal | Diazinon | Hexa- zinone | Methi- dathion | Meto- lachlor | Moli- nate | 0xy- fluorfen | Piper- onyl Butoxide | Sima- zine | Triflu- ralin |
|--------------------|------|-----------------|-------------------|---------|----------|-----------------|-------------------|------------------|---------------|------------------|----------------------------|---------------|------------------|
| Sampling year 2000 | | | | | | | | | | | | | |
| 02/12/00 | 1440 | nd | nd | nd | nd | _ | nd | nd | nd | _ | _ | nd | nd |
| 02/14/00 | 930 | 8.6 | 11.3 | 7.0 | 10.7 | | 20.1 | 11.7 | nd | _ | _ | 14.1 | 16.5 |
| 02/14/00 | 1615 | nd | nd | nd | nd | _ | nd | nd | nd | _ | | nd | nd |
| 02/19/00 | 1050 | nd | nd | nd | nd | | nd | nd | nd | _ | | nd | nd |
| | | | | | | | | | | | | | |
| | | | | | <u>S</u> | <u>ampling</u> | <u>year 2001</u> | <u>L</u> | | | | | |
| 01/19/01 | 1200 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 01/26/01 | 1245 | nd | nd | nd | nd | nd | nd | nd | 9.4 | nd | nd | nd | nd |
| 01/26/01 | 1745 | nd | nd | nd | nd | 10.0 | nd | nd | nd | nd | (2.9) | nd | nd |
| 01/30/01 | 1445 | nd | nd | nd | nd | nd | nd | nd | 14.9 | nd | nd | nd | nd |
| 02/04/01 | 1300 | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd | 17.7 |
| 02/05/01 | 1200 | nd | nd | nd | 12.0 | 17.3 | nd | nd | nd | 23.2 | 16.2 | 26.1 | 19.1 |

 Table 3.
 Pesticide concentrations in water samples collected at Orestimba Creek at River Road near Crows Landing, California, 2000–2001

[Values are reported as nanograms per liter. Water samples were analyzed for the following pesticides that were not detected at this site: alachlor, azinphosmethyl, carbofuran, cyanazine, fonofos, malathion, methylparathion, napropamide, pebulate, phosmet, sulfotep, and thiobencarb. nd, nondetection; —, not analyzed; (), concentration below detection limit]

| Date (mm/dd/yy) | Time | Atrazine | Butylate | Carbaryl | Chlorpyrifos | Cycloate | Dacthal | Diazinon | Diethatyl- ethyl | Eptam |
|--------------------|------|----------|----------|----------|---------------|----------|---------|----------|---------------------|-------|
| | | | | Sa | mpling year 2 | 000 | | | | |
| 01/30/00 | 1425 | nd | nd | nd | nd | nd | nd | 9.7 | nd | nd |
| 01/30/00 | 1625 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 02/11/00 | 2335 | nd | nd | nd | nd | nd | nd | 24.4 | nd | nd |
| 02/12/00 | 135 | nd | nd | nd | nd | nd | 17.2 | 24.5 | nd | nd |
| 02/12/00 | 300 | 11.4 | nd | nd | nd | nd | nd | 27.7 | nd | nd |
| 02/12/00 | 335 | nd | nd | nd | nd | nd | nd | 27.6 | nd | 19.3 |
| 02/12/00 | 630 | nd | nd | nd | nd | nd | 14.3 | 26.5 | nd | nd |
| 02/12/00 | 840 | nd | nd | nd | nd | nd | 15.5 | 25.1 | nd | nd |
| 02/12/00 | 1340 | nd | nd | nd | nd | nd | nd | 22.9 | nd | 16.8 |
| 02/13/00 | 2055 | nd | nd | nd | nd | nd | nd | 46.3 | nd | nd |
| 02/13/00 | 2130 | nd | nd | nd | nd | nd | 14.2 | 65.3 | nd | nd |
| 02/13/00 | 2320 | nd | nd | nd | nd | nd | nd | 252 | nd | nd |
| 02/14/00 | 030 | nd | nd | nd | nd | nd | nd | 71.4 | nd | nd |
| 02/14/00 | 130 | nd | nd | nd | nd | nd | nd | 93.2 | nd | nd |
| 02/14/00 | 230 | nd | nd | nd | 10.9 | nd | 6.3 | 61.7 | nd | nd |
| 02/14/00 | 650 | nd | nd | nd | nd | nd | 13.9 | 18.9 | nd | nd |
| 02/14/00 | 1100 | nd | 15.8 | nd | nd | nd | nd | 12.4 | nd | nd |
| 02/14/00 | 1500 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 02/15/00 | 1145 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 02/16/00 | 1200 | nd | nd | nd | nd | nd | nd | 13.3 | nd | nd |
| 02/17/00 | 615 | nd | nd | nd | nd | nd | nd | 14.3 | nd | nd |
| 02/17/00 | 1830 | nd | nd | nd | nd | nd | 6.0 | nd | nd | nd |
| 02/18/00 | 1300 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| 02/19/00 | 1000 | nd | nd | nd | nd | nd | nd | 14.4 | nd | nd |

Table 3. Pesticide concentrations in water samples collected at Orestimba Creek at River Road near Crows Landing, California, 2000–2001—Continued

| Date (mm/dd/yy) | Time | Atrazine | Butylate | Carbaryl | Chlorpyrifos | Cycloate | Dacthal | Diazinon | Diethatyl- ethyl | Eptam |
|--------------------|------|----------|----------|----------|---------------|----------|---------|----------|---------------------|-------|
| | | | | Sa | mpling year 2 | 001 | | | | |
| 01/19/01 | 1230 | 8.6 | nd | nd | nd | nd | nd | 9.9 | nd | nd |
| 01/25/01 | 1445 | nd | nd | nd | nd | nd | 196 | 18.4 | nd | nd |
| 01/25/01 | 1700 | 17.7 | nd | nd | nd | nd | nd | 11.9 | nd | nd |
| 01/25/01 | 1800 | nd | nd | nd | nd | nd | 8.5 | nd | 31.9 | nd |
| 01/25/01 | 1915 | 4.7 | nd | nd | nd | nd | nd | 7.8 | nd | nd |
| 01/25/01 | 2000 | (3.3) | nd | nd | nd | nd | 45.4 | 9.0 | nd | nd |
| 01/25/01 | 2100 | nd | nd | nd | nd | nd | nd | 11.0 | nd | nd |
| 01/25/01 | 2200 | 17.3 | nd | nd | nd | nd | 122 | 23.0 | nd | nd |
| 01/25/01 | 2300 | (3.1) | nd | nd | nd | nd | 82.3 | 8.3 | nd | nd |
| 01/25/01 | 2359 | 10.3 | nd | nd | nd | nd | 39.0 | 9.0 | nd | nd |
| 01/26/01 | 100 | 13.2 | nd | 22.6 | nd | nd | 38.9 | 12.8 | nd | nd |
| 01/26/01 | 200 | nd | nd | 19.2 | nd | nd | 45.0 | 7.8 | nd | nd |
| 01/26/01 | 300 | 18.4 | nd | nd | nd | nd | 15.7 | 15.7 | nd | nd |
| 01/26/01 | 400 | 10.3 | nd | nd | nd | nd | 22.6 | 18.7 | nd | 8.6 |
| 01/26/01 | 500 | 13.4 | nd | nd | nd | nd | 19.0 | 11.7 | nd | nd |
| 01/26/01 | 700 | 13.5 | nd | nd | nd | nd | 11.3 | 15.2 | nd | nd |
| 01/26/01 | 900 | 10.2 | nd | nd | nd | nd | 10.5 | 12.8 | nd | nd |
| 01/26/01 | 1845 | 9.4 | nd | nd | nd | 15.0 | 7.5 | 16.4 | nd | nd |
| 01/27/01 | 1830 | 10.8 | nd | nd | nd | nd | nd | 7.4 | nd | nd |
| 01/28/01 | 1520 | 18.1 | nd | nd | nd | nd | nd | 11.4 | nd | nd |
| 01/29/01 | 1430 | nd | nd | nd | nd | nd | 8.9 | 9.8 | nd | nd |
| 01/30/01 | 1530 | 10.9 | nd | nd | nd | nd | nd | 7.8 | nd | nd |
| 01/31/01 | 1051 | 10.0 | nd | nd | nd | nd | 8.3 | 18.4 | nd | nd |
| 02/01/01 | 1200 | 8.5 | nd | nd | 63.7 | nd | 8.4 | 49.6 | nd | nd |
| 02/05/01 | 1200 | 13.3 | nd | nd | nd | nd | 128 | 18.0 | nd | nd |

Table 3. Pesticide concentrations in water samples collected at Orestimba Creek at River Road near Crows Landing, California, 2000–2001—Continued

| Date (mm/dd/yy) | Time | Ethal- fluralin | Hexa- zinone | Methi- dathion | Meto- lachlor | Molinate | Pendi- methalin | Oxy- fluorfen | Piperonyl butoxide | Simazine | Trifluralin |
|--------------------|------|--------------------|-----------------|-------------------|------------------|----------|--------------------|------------------|-----------------------|----------|-------------|
| | | | | Samı | oling year | 2000 | | | | | |
| 01/30/00 | 1425 | nd | _ | 46.8 | 6.2 | nd | nd | _ | | 588 | 14.8 |
| 01/30/00 | 1625 | nd | _ | 43.5 | 104 | nd | nd | _ | | 963 | 29.0 |
| 02/11/00 | 2335 | nd | _ | nd | 14.5 | nd | 33.8 | _ | _ | 117 | 32.0 |
| 02/12/00 | 135 | 20.9 | _ | 9.4 | 226 | nd | 30.0 | _ | _ | 981 | 38.9 |
| 02/12/00 | 300 | nd | _ | (1.6) | 62.2 | nd | 20.0 | _ | _ | 104 | 18.8 |
| 02/12/00 | 335 | nd | _ | nd | 41.3 | nd | (10.5) | _ | _ | 366 | 23.2 |
| 02/12/00 | 630 | nd | _ | 9.4 | 44.3 | nd | 30.1 | _ | _ | 196 | 23.2 |
| 02/12/00 | 840 | nd | _ | 9.9 | 52.0 | nd | 28.7 | _ | _ | 362 | 27.8 |
| 02/12/00 | 1340 | nd | _ | nd | 22.8 | nd | 40.4 | _ | _ | 283 | 24.6 |
| 02/13/00 | 2055 | nd | _ | 92.3 | 9.8 | nd | 22.3 | _ | _ | 182 | 23.1 |
| 02/13/00 | 2130 | nd | _ | 95.2 | 38.0 | nd | 40.6 | _ | _ | 191 | 27.0 |
| 02/13/00 | 2320 | nd | | 25.2 | 10.4 | nd | nd | _ | | 70.0 | 30.3 |
| 02/14/00 | 030 | nd | _ | 61.0 | 35.3 | nd | nd | _ | _ | 83.4 | 41.4 |
| 02/14/00 | 130 | nd | _ | 31.8 | nd | nd | nd | _ | _ | nd | 25.5 |
| 02/14/00 | 230 | nd | | 30.0 | 12.9 | nd | 22.3 | _ | | 58.3 | 17.1 |
| 02/14/00 | 650 | nd | _ | nd | nd | nd | nd | _ | _ | 31.7 | 19.3 |
| 02/14/00 | 1100 | nd | _ | nd | nd | nd | nd | _ | _ | nd | 21.8 |
| 02/14/00 | 1500 | nd | _ | nd | nd | nd | nd | _ | _ | 33.9 | 6.1 |
| 02/15/00 | 1145 | nd | _ | nd | 11.5 | nd | nd | _ | | nd | 11.3 |
| 02/16/00 | 1200 | nd | | nd | nd | nd | nd | _ | _ | 57.0 | 12.5 |
| 02/17/00 | 615 | nd | | nd | nd | nd | nd | _ | _ | 30.7 | 13.3 |
| 02/17/00 | 1830 | nd | | nd | 8.4 | nd | 14.9 | _ | _ | nd | 13.5 |
| 02/18/00 | 1300 | nd | | nd | nd | nd | nd | _ | _ | nd | 21.7 |
| 02/19/00 | 1000 | nd | _ | nd | nd | nd | nd | _ | _ | 21.3 | 13.0 |

Table 3. Pesticide concentrations in water samples collected at Orestimba Creek at River Road near Crows Landing, California, 2000–2001—Continued

| Date (mm/dd/yy) | Time | Ethal- fluralin | Hexa- zinone | Methi- dathion | Meto- lachlor | Molinate | Pendi- methalin | Oxy- fluorfen | Piperonyl butoxide | Simazine | Trifluralin |
|--------------------|------|--------------------|-----------------|-------------------|------------------|--------------|--------------------|------------------|-----------------------|----------|-------------|
| | | | | Samp | ling year 2 | <u> 2001</u> | | | | | |
| 01/19/01 | 1230 | nd | 43.6 | nd | 9.6 | nd | 8.8 | 40.1 | nd | 62.5 | 25.1 |
| 01/25/01 | 1445 | nd | 47.5 | nd | 31.5 | nd | 27.8 | 49.2 | nd | 74.1 | 24.4 |
| 01/25/01 | 1700 | nd | 45.1 | nd | 16.1 | nd | 25.5 | 38.3 | nd | 54.4 | 16.1 |
| 01/25/01 | 1800 | nd | 56.2 | nd | 23.1 | nd | 38.9 | 60.9 | 24.7 | 54.4 | 36.8 |
| 01/25/01 | 1915 | nd | 55.9 | nd | 10.2 | nd | 27.2 | 46.3 | nd | 45.2 | 27.6 |
| 01/25/01 | 2000 | nd | 47.8 | nd | 34.3 | nd | 30.3 | 42.2 | nd | 58.2 | 17.4 |
| 01/25/01 | 2100 | nd | 49.8 | nd | 12.1 | nd | 25.5 | 44.8 | nd | 41.0 | 24.1 |
| 01/25/01 | 2200 | nd | 38.3 | nd | 23.0 | nd | 26.0 | 39.3 | nd | 67.6 | 16.0 |
| 01/25/01 | 2300 | nd | 43.0 | nd | 16.3 | nd | 27.8 | 37.2 | nd | 116 | 22.3 |
| 01/25/01 | 2359 | nd | 35.1 | nd | 6.7 | nd | 22.5 | 28.6 | 11.6 | 129 | 9.7 |
| 01/26/01 | 100 | nd | 61.4 | nd | 20.7 | nd | 24.1 | 49.7 | nd | 242 | 19.1 |
| 01/26/01 | 200 | nd | 72.0 | nd | 54.6 | nd | 61.6 | 114 | nd | 315 | 18.4 |
| 01/26/01 | 300 | nd | 59.4 | nd | 29.1 | nd | 41.1 | 97.2 | nd | 337 | 17.0 |
| 01/26/01 | 400 | nd | 39.5 | nd | 21.5 | 12.3 | 27.1 | 52.4 | nd | 330 | 19.9 |
| 01/26/01 | 500 | nd | 35.3 | nd | 19.0 | nd | 24.6 | 51.7 | nd | 301 | 19.4 |
| 01/26/01 | 700 | nd | 41.8 | nd | 11.9 | nd | 31.3 | 64.2 | 8.9 | 236 | 14.6 |
| 01/26/01 | 900 | nd | 38.6 | nd | 15.2 | nd | 22.4 | 40.7 | nd | 145 | 17.4 |
| 01/26/01 | 1845 | nd | 39.0 | nd | 21.2 | nd | 20.5 | 168 | nd | 75.8 | 17.7 |
| 01/27/01 | 1830 | nd | 40.1 | nd | 6.2 | nd | nd | 87.6 | 13.1 | 1,611 | 12.1 |
| 01/28/01 | 1520 | nd | 40.6 | nd | 16.3 | nd | 111 | 78.9 | nd | 321 | 17.0 |
| 01/29/01 | 1430 | nd | 34.7 | nd | 16.6 | nd | 31.5 | 40.9 | nd | 60.5 | 18.6 |
| 01/30/01 | 1530 | nd | 41.7 | nd | 4.9 | nd | 26.7 | 33.5 | nd | 62.4 | 8.3 |
| 01/31/01 | 1051 | nd | 53.4 | nd | 14.8 | nd | 33.8 | 30.5 | 5.2 | 50.3 | 10.3 |
| 02/01/01 | 1200 | nd | 29.0 | nd | 14.3 | nd | 33.0 | 30.2 | nd | 48.1 | 10.6 |
| 02/05/01 | 1200 | nd | 26.0 | nd | 25.1 | nd | 28.8 | 33.8 | nd | 90.2 | 12.7 |

Table 4. Pesticide concentrations in water samples collected at San Joaquin River near Vernalis, California, 2000–2001

[Values are reported as nanograms per liter. Water samples were analyzed for the following pesticides that were not detected at this site: alachlor, azinphosmethyl, butylate, carbofuran, cyanazine, cycloate, eptam, fonofos, malathion, methylparathion, molinate, pebulate, sulfotep, and thiobencarb. nd, nondetection; —, not analyzed; (), concentration below detection limit]

| Date (mm/dd/yy) | Time | Atrazine | Carbaryl | Chlor- pyrifos | Dacthal | Diazinon | Diethatyl- ethyl | Ethal- fluralin | Hex- azinone | Methi- dathion | Meto- lachlor |
|--------------------|------|----------|----------|-------------------|----------|-----------|---------------------|--------------------|-----------------|-------------------|------------------|
| | | | | | Sampling | year 2000 | | | | | |
| 01/24/00 | 1500 | nd | nd | nd | nd | 7.6 | nd | nd | _ | 44.8 | (2.1) |
| 01/25/00 | 010 | nd | nd | nd | nd | 9.3 | nd | nd | _ | nd | nd |
| 01/25/00 | 1100 | nd | nd | nd | nd | 11.5 | nd | nd | _ | 51.4 | (3.6) |
| 01/25/00 | 2000 | nd | nd | nd | nd | 26.8 | nd | nd | _ | nd | 19.3 |
| 01/26/00 | 730 | nd | nd | nd | nd | 14.8 | nd | nd | _ | nd | 4.6 |
| 01/27/00 | 820 | nd | nd | nd | nd | nd | nd | nd | _ | nd | nd |
| 01/27/00 | 1600 | nd | nd | nd | nd | nd | nd | nd | _ | nd | nd |
| 02/11/00 | 2200 | 10.2 | nd | nd | nd | 26 | nd | nd | _ | (0.3) | 15.6 |
| 02/12/00 | 1230 | 11.0 | nd | nd | nd | 21.8 | nd | nd | _ | (0.6) | 15.1 |
| 02/12/00 | 2100 | 10.0 | nd | nd | nd | 31.2 | nd | nd | _ | nd | 6.3 |
| 02/13/00 | 530 | 13.1 | nd | nd | nd | 77.1 | nd | nd | _ | (1.1) | 35.3 |
| 02/13/00 | 2330 | 8.8 | nd | nd | nd | 40.6 | nd | nd | _ | (3.9) | 18.6 |
| 02/14/00 | 650 | 11.5 | nd | nd | nd | 40.7 | nd | nd | _ | (0.9) | 26.2 |
| 02/14/00 | 2000 | nd | nd | nd | nd | 35.6 | nd | nd | _ | 33.2 | 21.7 |
| 02/15/00 | 900 | nd | nd | 12.3 | nd | 22.5 | nd | nd | _ | nd | 13.2 |
| 02/15/00 | 1000 | nd | nd | nd | nd | 26.4 | nd | nd | _ | nd | nd |
| 02/15/00 | 1830 | nd | nd | 18.0 | nd | 17.1 | nd | nd | _ | nd | 18.7 |
| 02/16/00 | 830 | nd | nd | nd | nd | 13.5 | nd | nd | _ | nd | 4.2 |
| 02/16/00 | 1600 | nd | nd | nd | nd | 17.9 | nd | (0.8) | _ | nd | nd |
| 02/16/00 | 1945 | nd | nd | nd | nd | nd | nd | nd | _ | nd | nd |
| 02/17/00 | 930 | nd | nd | nd | nd | 23.4 | nd | nd | _ | nd | nd |
| 02/17/00 | 1930 | nd | nd | nd | nd | 16.2 | nd | nd | _ | nd | nd |
| 02/18/00 | 1005 | nd | nd | nd | nd | 13.4 | nd | nd | _ | nd | nd |
| 02/18/00 | 1930 | 11.4 | nd | nd | nd | nd | nd | nd | _ | nd | nd |
| 02/19/00 | 830 | nd | nd | nd | nd | 12.6 | nd | nd | _ | nd | 15.7 |
| 02/23/00 | 1200 | 12.1 | nd | nd | nd | nd | nd | nd | _ | nd | nd |
| 02/23/00 | 1200 | nd | nd | nd | nd | 10.7 | nd | nd | _ | nd | (3.5) |
| | | | | | Sampling | year 2001 | | | | | |
| 01/19/01 | 1330 | (1.3) | nd | 16.3 | nd | 6.5 | nd | nd | 30.2 | nd | nd |
| 01/26/01 | 1345 | 16.0 | nd | 18.2 | 10.4 | 39.3 | nd | nd | 32.5 | 33.0 | 22.3 |
| 01/27/01 | 845 | 10.7 | 31.6 | nd | nd | 133 | nd | nd | 27.9 | 17.6 | nd |
| 01/27/01 | 1710 | nd | 27.5 | nd | nd | 128 | 32.0 | nd | 55.1 | 29.0 | 25.6 |
| 01/28/01 | 1030 | 19.3 | nd | nd | nd | 134 | nd | nd | 37.8 | nd | 19.1 |
| 01/28/01 | 1650 | 8.6 | nd | 14.6 | nd | 154 | nd | nd | 34.4 | 26.0 | 16.8 |
| 01/29/01 | 915 | nd | nd | 13.4 | nd | 126 | nd | nd | 32.5 | nd | 12.3 |
| 01/29/01 | 930 | 16.0 | nd | nd | nd | 137 | nd | nd | 39.2 | nd | 18.9 |
| 01/29/01 | 2020 | 7.8 | nd | 13.6 | nd | 113 | nd | nd | 44.7 | nd | 16.2 |
| 01/30/01 | 1800 | nd | nd | nd | nd | 103 | nd | nd | 106 | nd | 19.4 |
| 01/31/01 | 800 | nd | nd | nd | nd | 52.9 | nd | nd | 105 | nd | 6.1 |
| 02/01/01 | 1100 | nd | 8.3 | 8.2 | nd | 33.3 | nd | nd | 47.3 | nd | 11.1 |
| 02/04/01 | 1200 | nd | 20.9 | nd | nd | 22.4 | nd | nd | 28.7 | nd | 18.6 |

 Table 4.
 Pesticide concentrations in water samples collected at San Joaquin River near Vernalis, California, 2000–2001—Continued

| Date (mm/dd/yy) | Time | Napropamide | Pendimethalin | Phosmet | Oxyfluorfen | Piperonyl butoxide | Simazine | Triflurali |
|--------------------|------|-------------|---------------|--------------|-------------|-----------------------|----------|------------|
| | | | | Sampling yea | r 2000 | | | |
| 01/24/00 | 1500 | nd | 35.1 | nd | | | 95.0 | 15.6 |
| 01/25/00 | 010 | nd | 35.3 | nd | | | 80.8 | 15.6 |
| 01/25/00 | 1100 | nd | 42.9 | 53.9 | | | 123 | 17.3 |
| 01/25/00 | 2000 | nd | 37.9 | nd | _ | _ | 244 | nd |
| 01/26/00 | 730 | nd | 36.2 | nd | _ | _ | 149 | nd |
| 01/27/00 | 820 | nd | 37.2 | nd | | | 136 | nd |
| 01/27/00 | 1600 | nd | 40.3 | nd | _ | _ | 99.6 | nd |
| 02/11/00 | 2200 | nd | 16.8 | nd | _ | _ | 45.2 | 15.8 |
| 02/12/00 | 1230 | nd | 13.3 | nd | | | 35.4 | 15.8 |
| 02/12/00 | 2100 | nd | 25.7 | nd | _ | _ | 206 | 14.7 |
| 02/13/00 | 530 | nd | 28.6 | nd | _ | | 106 | 21.3 |
| 02/13/00 | 2330 | nd | 18.8 | nd | _ | | 448 | 16.6 |
| 02/14/00 | 650 | nd | 22.6 | nd | _ | | 469 | 20.6 |
| 02/14/00 | 2000 | 28.4 | nd | nd | _ | | 471 | nd |
| 02/15/00 | 900 | 38.9 | 17.5 | nd | _ | | 461 | 13.1 |
| 02/15/00 | 1000 | 37.3 | 20.7 | nd | _ | | 470 | 13.7 |
| 02/15/00 | 1830 | nd | 36.0 | nd | _ | | 487 | 6.4 |
| 02/16/00 | 830 | 45.7 | nd | nd | _ | | 435 | nd |
| 02/16/00 | 1600 | 12.7 | 17.9 | nd | _ | | 331 | 14.5 |
| 02/16/00 | 1945 | nd | 43.2 | nd | _ | | 304 | 6.4 |
| 02/17/00 | 930 | nd | 19.6 | nd | _ | | 166 | 10.8 |
| 02/17/00 | 1930 | nd | 18.4 | nd | _ | | 133 | 11.5 |
| 02/18/00 | 1005 | nd | nd | nd | _ | | 113 | 9.8 |
| 02/18/00 | 1930 | nd | 23.6 | nd | _ | | 157 | 13.7 |
| 02/19/00 | 830 | nd | nd | nd | _ | | 124 | 6.7 |
| 02/23/00 | 1200 | nd | 23.5 | nd | _ | | 122 | 14.4 |
| 02/23/00 | 1200 | nd | nd | nd | _ | _ | 63.6 | nd |
| | | | | Sampling yea | ır 2001 | | | |
| 01/19/01 | 1330 | nd | 24.1 | nd | nd | 19.6 | 51.1 | 21.4 |
| 01/26/01 | 1345 | nd | 27.3 | nd | 25.0 | 19.6 | 111 | 18.3 |
| 01/27/01 | 845 | nd | 39.0 | nd | nd | 15.1 | 179 | 8.1 |
| 01/27/01 | 1710 | nd | 72.7 | nd | 57.7 | 28.2 | 178 | 35.4 |
| 01/28/01 | 1030 | 90.7 | 64.2 | nd | nd | nd | 376 | nd |
| 01/28/01 | 1650 | 79.8 | 39.8 | nd | nd | nd | 372 | 16.3 |
| 01/29/01 | 915 | 62.7 | 35.0 | nd | nd | 4.5 | 694 | 10.5 |
| 01/29/01 | 930 | 67.7 | 40.7 | nd | nd | nd | 731 | nd |
| 01/29/01 | 2020 | 34.0 | 32.9 | nd | nd | 12.6 | 664 | 16.0 |
| 01/30/01 | 1800 | nd | 26.3 | nd | nd | 16.6 | 468 | 19.7 |
| 01/31/01 | 800 | nd | 25.7 | nd | nd | 14.0 | 453 | 8.6 |
| 02/01/01 | 1100 | nd | 22.3 | nd | nd | 10.5 | 211 | 11.3 |
| 02/04/01 | 1200 | nd | 23.5 | nd | nd | 3.9 | 79.0 | 9.0 |

Table 5. Method detection limits for pesticides analyzed in 2000 and 2001

[—, not analyzed]

| Pesticide | 2000 Method detection limit, in nanogram per liter | 2001 Method detection limit, in nanogram per liter | |
|------------------------------|--|--|--|
| Alachlor ¹ | 3.8 | 2.1 | |
| Atrazine | 4.3 | 4.2 | |
| Azinphos-methyl ¹ | _ | 11.1 | |
| Butylate | 4.5 | 1.8 | |
| Carbaryl | 4.6 | 4.2 | |
| Carbofuran | 5.5 | 3.3 | |
| Chlorpyrifos | 1.5 | 4.2 | |
| Cyanazine1 | _ | 3.0 | |
| Cycloate | 2.2 | 1.5 | |
| Dacthal | 1.5 | 1.2 | |
| Diazinon | 2.0 | 3.6 | |
| Diethatyl-ethyl | 2.2 | 3.6 | |
| Eptam | 5.7 | 4.5 | |
| Ethalfluralin | 5.0 | 2.4 | |
| Fonofos ¹ | 3.5 | 2.4 | |
| Hexazinone | _ | 5.7 | |
| Malathion ¹ | 3.1 | 2.1 | |
| Methidathion | 5.5 | 5.4 | |
| Methylparathion ¹ | 6.9 | 4.2 | |
| Metolachlor | 4.0 | 3.3 | |
| Molinate | 4.0 | 2.7 | |
| Napropamide | 10.9 | 7.2 | |
| Oxyfluorfen | _ | 4.2 | |
| Pebulate ¹ | 3.4 | 0.6 | |
| Pendimethalin | 12.4 | 2.4 | |
| Phosmet | 5.9 | 4.2 | |
| Piperonyl butoxide | _ | 3.3 | |
| Simazine | 5.2 | 6.9 | |
| Sulfotep ¹ | 2.0 | 1.2 | |
| Thiobencarb ¹ | 3.4 | 3.9 | |
| Trifluralin | 3.1 | 3.0 | |

¹Pesticide not detected in any samples in either year.

Significant figures were estimated by the rounding method as described in American Society for Testing and Materials (1993).

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